THE CHEMICAL AND PHYSICAL PROPERTIES OF THE DIENE ADDITION PRODUCTS TO DIAROYLETHYLENES

BY

MARVIN HAROLD GOLD

A. B., University of California at Los Angeles, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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Introduction

In this investigation several conjugated dienes were added to *trans*-dibenzoylethylene and *trans*-dixenoylethylene. The products so obtained, were used as intermediates in the preparation of 4,7-dihydroisobenzofurans, isobenzofurans and *o*-diaroylbenzenes. The furans became of further interest because of their intense fluorescence. This led to an investigation of their absorption and fluorescence spectra.

Historical

1,3-Diphenylisobenzofuran was first reported by Guyot and Catel[1], who prepared it by the action of phenylmagnesium bromide on phenylphthalide. Blicke and Weinkauff,[2] found that 1,3-di-(hydroxy or methoxy)-phenylisobenzofurans could be produced by the action of concentrated sulfuric acid on the corresponding phthalin.

The isobenzofurans are easily oxidized to *o*-dibenzoylbenzenes and here-to-fore this has been the best and most general method of preparation.

Boyd and Ladhams[3], and Blicke and Patelski[4], showed that *o*-diaroylbenzenes could be converted to 1,3-diarylisobenzofurans by means of zinc dust and acetic acid.

Discussion of Results

Butadiene and 2,3-dimethylbutadiene were condensed with *trans*-dibenzoylethylene and *trans*-dixenoylethylene to give quantitative or nearly quantitative yields of 4,5-diaroyl or 1,2-dimethyl-4,5-diaroylcyclohexenes. These were quantitatively converted to 1,3-diaryl-4,7-dihydroisobenzofurans by means of a few drops of syrupy phosphoric acid as a catalyst, in acetic anhydride solution.

The dihydroisobenzofurans upon treatment with two moles of bromine followed by sodium acetate in acetic acid produced *o*-diaroylbenzenes in 80 to 90 per cent yields. In this manner, by using the proper butadiene, 1,2-dialkyl or diaryl-4,5-diaroylbenzenes, which are not readily available by other means, can easily be prepared.

Since in the reactions here-in described, the *o*-diaroylben-

zenes are more easily obtained than the isobenzofurans, the conversion of the former to the latter was investigated. It was found that activated zinc dust and ethanolic alkali was an excellent reagent for the reduction to produce 1,3-diarylisobenzofurans.

1,3-Diphenyl-5,6-dimethylisobenzofuran also has an active conjugated diene system. This fact was utilized in its condensations with both maleic anhydride and *trans*-dibenzoylethylene to produce the corresponding 1,4-oxido-substituted-1,2,3,4-tetrahydronaphthalenes. These in turn could be readily transformed into substituted naphthalenes by treatment with hydrogen chloride in boiling alcohol.

The 4,7-dihydroisobenzofurans also add maleic anhydride but in this case the reaction is so reversible that pure products cannot be isolated.

Cyclopentadiene was added to both the *cis* and *trans* forms of dibenzoylethylene to produce the two isomeric 2,3-dibenzoyl-1,4-endomethylene-1,2,3,4-tetrahydrobenzenes. These could not be converted to the dihydroisobenzofurans by the procedure used for the cyclohexene derivatives.

The fluorescence and absorption spectra of the isobenzofurans and the dihydroisobenzofurans were studied. In general the spectra of the isobenzofurans and the dihydroisobenzofurans are similar within their own groups. For either type of structure a wide absorption band occurs in the near ultraviolet. It is this absorption band in which energy is obtained to excite the fluorescence emission. The effect of the substitution of xenyl for phenyl groups, is to shift the band maxima to longer wave lengths. Methyl groups have a negligible effect.

It appears likely that as a possible mechanism, the fluorescence emission occurs through a transitory free radical stage. The ease of activation of this form, can be assigned to a possible stabilization proportional to number of resonance structures. This number varies with the type of aromatic substituents on the isobenzofuran nucleus.

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VITA

The writer was born in Buffalo, New York, on June 23, 1915. He attended the public schools of that city until January, 1930, and then moved to Los Angeles, California, where he was graduated from Manual Arts High School in June, 1933. The following September he enrolled in the University of California at Los Angeles and was granted the degree of Bachelor of Arts from that institution in June, 1937. In the fall of the same year he entered the Graduate School of the University of Illinois.